Conference Paper

Leaching of Waste Hydroxide Sludges by Complex-Forming Agents

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Abstract

In the paper the problem of utilization of stale hydroxide sludges containing non-ferrous metals and arsenic is considered. It is proposed to carry out two-stage leaching of sludges by solutions of complexing agents with recovery of 97-99% of non-ferrous metals to solution and removal of arsenic in the form of sparingly soluble compounds suitable for burial.

Keywords: leaching, hydroxide sludges, EDTA, complexation, arsenic containing waste

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1. Introduction

Annually at the enterprises of nonferrous metallurgy a large amount of solid waste products containing valuable components are produced. One of such wastes are sludges obtained by neutralization of substandard technological solutions of electrolysis and hydrometallurgical shops of copper production enterprises.

At copper-refining plants, schemes for processing of spent electrolytes to produce copper and nickel sulfates are widely used. But relatively large capital costs for the organization of vitriol production make the one unprofitable for enterprises with a low annual output. Thus, an affordable alternative is the way of treatment substandard solutions by neutralization with lime milk. As a result, a large amount of sludge is formed, consisting mainly of gypsum, hydroxides of non-ferrous metals and iron, as well as arsenic compounds. The copper content in the sludge achieves 10%, nickel up to 9%, while the arsenic content is 0.5-3%.

Due to complexity of chemical and mineralogical compositions, processing of such sludge for enterprises becomes burdensome, therefore sludges are directed to the sludge pond. Implementation of pyrometallurgical methods for processing of such materials requires large energy consumption, the utilization of highly toxic dusts and gases generated and does not provide the selectivity of extraction of non-ferrous metals.

Involvement in the processing of accumulated sludge, which is a promising anthropogenic raw material, allows extracting valuable components (copper, nickel) in a quality and demanded product. This also ensures reduction of the volume of stored high-toxic solid waste. Arsenic should be removed in the form of sparingly soluble compounds suitable for long-term storage.

Applying of hydrometallurgical methods for the processing of solid multicomponent materials makes it possible to provide the recovery of valuable components to a solution, acceptable for further processing. Dissolving of metal hydroxides does not any technological complications, and can be carried out by treating the sludge by solutions of mineral acids [1] (mainly sulfuric acid), which provides a high degree of metal recovery.

Metals can be completely transferred from the solid phase to the solution by sulfuric acid - available and inexpensive reagent. However, at applying of sulfuric acid leaching, arsenic also passes into solution. Thus, it is necessary to include in the scheme the stage of selective removal of non-ferrous metals from solutions containing a significant amount of arsenic.

Separation of non-ferrous metals and arsenic, which are collectively present in solutions, can be successfully carried out by sorption and extraction processes, cementation, etc. [2–6]. However, these methods have a number of technological limitations, additionally, the spent arsenic-containing solutions require special treatment.

A method of arsenic removal in the form of calcium arsenate including precipitation of dissolved arsenic by lime milk $Ca(OH)_2$ is widely known [7]. Method of arsenic precipitation is not suitable due to incomplete precipitation and certain solubility of the formed compound, as a result arsenic dissolve into groundwater and adversely effects on the environment. Therefore, the scheme of hydroxide sludges leaching by sulfuric acid has some disadvantages and difficult to implement.

It is reasonable to assure the transfer of non-ferrous metals to solution, while retaining arsenic in a gypsum cake. In a number of works, a solution of complexing agents for the selective removal and precipitation of non-ferrous metals has been recommended [8, 9]. Thus, the use of complexing reagents is promising for the leaching of stale hydroxide sludges.

Ligand	Complex	Cu(II)	Ni(II)	Ca(II)
edta	$Me(edta)^{2-}$	18,8	18,62	10,7
	$Me(Hedta)^{-}$	11,54	11,56	3,51

Table 1: Constants of stability of copper, nickel and calcium complexes.

2. Experimental

Trilon B as complexing agent was used. The complexing agent was chosen with taken into account the possibility of reagent regeneration [10] and forming of stable complexes with non-ferrous metals [11]. Stability of trilon B compounds with Me^{n+} is not the same and depends on the ratio of the metal:ligand and the pH of the solution (Table 1).

It is known, that in trilonate solutions Cu(II) and Ni(II) present, mainly, as anionic complexes CuY^{2-} and NiY^{2-}, where Y^{4-} – edta anion. The use of Trilon B, on the one hand, provides the transfer of non-ferrous metals into a solution with a high degree of recovery, but at the same time limits the applicability of certain methods of solutions processing (electrowinning, cementation).

One of the methods of the complexing agent regeneration is to precipitate EDTA from trilonate solutions by interacting them with solutions of mineral acids. The solubility of EDTA is minimal at pH 1.4-1.6. Thus, by decreasing the pH of the solution after leaching to 1.5 units, it is possible to destruct the metal complexes with the simultaneous regeneration of the complexing agent (EDTA) [10]. Non-ferrous metals at the destruction of the trilonate complex in an acidic medium exist in solution in the form of cations.

Experiments on the leaching of copper and nickel hydroxides with the simultaneous presence of arsenic were carried out using synthetic slurry. The sludge was obtained by treatment of a solution of $NiSO_4 \cdot 7H_2O$, $CuSO_4 \cdot 5H_2O$ salts by lime milk with the addition of arsenious acid.

As a result, a precipitate containing of hydroxides of copper and nickel, calcium arsenite and gypsum was obtained. Chemical composition of synthetic hydrated sludge is, %: 6.92 Cu, 6.62 Ni, 24.48 Ca, 1.2 As. A series of experiments was conducted to study the effect of the ratio of the amount of complexing agent to the amount of non-ferrous metals in the sludge, the initial pH and the temperature to the degree of extraction of non-ferrous metals and arsenic.

In solution of trilon B with concentration 75 g/dm^3 and volume 150 cm^3 an initial pH = 1,5-4,5 was adjusted by adding of sulfuric acid. Air-dried synthetic sludge was ground and necessary mass of sludge was added to trilon B solution to the required ratio L:S

Temperature, [°C]	L:S	$pH_{initial}$	pH_{final}	Recovery of sum of non-ferrous metal, [%]	Recovery of arsenic, [%]
20	9.99	4.56	11.33	18.68	0
20	10.00	1.5	4.48	98.54	88.12
52	7.50	3.06	8.36	27.48	0.4
52	11.91	3.03	8.84	43.21	0.3
52	7.48	1	9.78	82.04	0
52	7.49	0.49	4.21	71.94	92.68
80	9.98	1.51	4.77	84.02	84.12

Table 2: Leaching conditions.

= 1:(5; 7,5; 10). Duration of contact is 2 hours at temperature 20-80 °C and mechanical mixing. Conditions and results are shown in the Table 2.

Changing in the ratio of the amount of sludge to the volume of the trilonate solution makes it possible to vary the range of pH during the leaching process, which allows one to evaluate the effect of equilibrium pH on the selective extraction of non-ferrous metals. From the data in Table 2 it is follows that the crucial parameter affecting the extraction of elements is the pH of the solution. It was found that at initial pH $\leq$ 1.5, the maximum extraction of non-ferrous metals occurs. At a final pH> 8, a considerable decreasing in the solubility of arsenic is observed.

Thus, solutions of EDTA salts allow to extract non-ferrous metals from the sludge without contaminating the solution by arsenic.

3. Conclusions

Experiments for selection of optimal leach conditions by EDTA solutions have shown the possibility of achieving a copper recovery of up to 77 % and nickel up to 86 %, while arsenic in not dissolve. At the same time, the trilonate leaching provides the maximum possible recovery for copper up to 99 % and for nickel up to 97 %, with simultaneously complete transferring arsenic to the solution (96 %). Thus, it is reasonable to carry out the leaching of the sludge in a two-step process, which will make it possible to achieve selectivity at non-ferrous metals dissolution and them maximum extraction. Implementation of leaching at pH > 8 allows almost completely eliminating the transfer of arsenic to the solution. The obtained data make it possible to conclude that the use of EDTA solutions for leaching sludges of neutralization of industrial solutions is promising.

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